



ATTACHMENT B

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

FIRST NAMED APPLICANT

U.S. Application Serial No.

: Kevin D. Belfield

: 10/821,755 Continuation-in-part Application of SN 10/306,960 filed
11/27/2002, now U.S. Patent 7,001,708

Filed

: 04/09/2004

For

: TWO-PHOTON FLUORESCENT TERNARY OPTICAL DATA
STORAGE

Attorney Docket

: UCF-385

DECLARATION UNDER 37 C.F.R. 1.131

Honorable Commissioner for Patents

P.O. Box 1450

Alexandria, VA 22313-1450

Sir:

The inventor listed below declares that he is the inventor on the above referenced patent application, who on April 09, 2004 filed the above identified patent application which is a continuation-in-part application of patent application 10/306,960 filed November 27, 2002, which claims the benefit of priority to United States Provisional patent application 60/339,283 filed December 11, 2001, and United States Provisional patent application 60/333,972, filed on November 28, 2001. The inventor further declares that the claimed invention to two-photon fluorescence in binary and ternary Optical Data Storage in the subject patent application was reduced to practice well before December 20, 2001, which is the effective date of the publication of Fleming et al., WO 01/96959, "Multidirectional Photoreactive Absorption Method," International Publication Date: December 20, 2001.

The inventor declares that attached to this declaration are copies of two Invention Disclosure Forms (IDF) prepared by the inventor, Kevin D. Belfield. The IDF dated September 24, 2001 provides evidence that the claimed invention for two-photon fluorescent binary optical data storage was reduced to practice at least as early as October 2000 (Exhibit A). Another IDF dated November 18, 2002 provides evidence that the claimed invention for two-photon fluorescence ternary optical data storage was reduced to practice at least as early as May 2002 (Exhibit B). Together, the two IDF submissions provide evidence that the subject matter of claim 1, namely a "method of writing data in a WORM (Write Once Read Many Times) optical data storage with two-photon fluorescent readout" was reduced to practice at least as early as October 2000 for binary code storage and is the basis of priority for the invention claiming ternary code data storage and is well before the date of December 20, 2001, which is the effective date of the Fleming et al. reference.

The inventor further declares that he does not know and does not believe that his invention was made public more than one year prior to this application being first filed as a Provisional Patent Application 60/339,283 on December 11, 2001 and Provisional Patent Application 60/333,972, filed on November 28, 2001.

The inventor further declares that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Respectfully Submitted:

Kevin D. Belfield

Date

Date and hour of receipt:

9/24/2011 11:00 am JMW

University of Central Florida Invention Disclosure Form

1. Title of invention: (Brief, but comprehensive, technically accurate and descriptive)

New Photosensitive Material for WORM Optical Data Storage with Two-Photon Fluorescent Readout

2. Inventors: (Full name, title, nationality, address (work and home), phone of inventor or inventors)

a. Kevin D. Belfield, Associate Professor, work: Dept. of Chemistry,
University of Central Florida P.O. Box 162366, Orlando, FL 32816 nationality USA

home: 2231 Westbourne Dr.

Oviedo, FL 32765

nationality

c.

nationality

d.

nationality

3. Financial Support/Contract Identification: Identify the specific grant or contract number (not the account number) and the external sponsors (governmental agencies, industrial sponsors, private agencies, or others) which provided support used to defray the costs related to the research from which the invention resulted. This information is needed to determine whether this invention is subject to any commitments or restrictions arising from the terms of sponsorship.

none

4. List any existing agreements regarding this technology. Identify any and all agreements involving this technology. To include: research agreements, confidential disclosure agreements, consulting agreements, material transfer agreements, visiting scientist agreements or other agreements which are in place.

none

5. Concise description of the invention: Your disclosure should enable someone having knowledge of the field to understand the invention. Include all essential elements (features, concepts, or new results of the invention, whichever is most applicable), their relationship to one another, and their mode of operation. Identify the elements which are considered novel. Also, if the invention is an apparatus or system, attach drawings or a sketch and indicate if it has ever been built or tested. Use additional pages if necessary, attach drawings, manuscripts, papers, or other supporting material to facilitate understanding of the invention.

A photosensitive polymeriz. material was prepared and used to demonstrate 3-D optical data storage. Recording by conventional UV-visible exposure and photolithography ~~or~~ two-photon near IR excitation was demonstrated. 3-D readout of multilayer media was demonstrated using two-photon upconverted fluorescence detection. Both positive and negative image formation is possible (was demonstrated). multichannel

6. **Background:** In order for patent counsel to determine the patentability of this invention, it will be necessary to compare it to existing technology (referred to as "prior art"). This section should provide information to aid in the evaluation.

- a. List any published material such as patents, commercial literature, scientific articles relating to the invention.
- b. Identify the advantages or benefits of the invention over currently available technology, such as efficiency, cost benefit, simplicity, overcoming a defeat.
- c. Identify possible uses or new uses of the invention.
- d. What is the deficiency in the prior art which your invention improves upon, or the limitation which it extends.

see attached

7. Date and place at which discovery was made:

10/2000 University of Central Florida

8. Names and addresses of persons familiar with your work on this invention

Katherine J. Schaefer

Eric W. Van Styland

9. What do you see as the commercial use of your invention?

a possible optical data storage medium + process

10. What firms/companies do you think may be, or are, interested in it; and why?

CallRecall - developing 3-D optical data storage materials

11. What do you see as the greatest impediment to the adoption of your invention?

- integration by current technology

12. Public Disclosure/ Publication Plans: Public disclosure involves abstracts, and presentations at scientific meetings (including poster sessions), public seminars, shelving of thesis, publications, disclosure to others outside the University who have not signed a confidentiality agreement, and use, sale, or offer of sale of the invention. Identify dates and circumstances of any such disclosures. Also, indicate your future disclosure or publication plans, and notify the Office of Technology Transfer if the invention becomes publicly disclosed or published (whether by plan or inadvertently).

Submitted paper to Chemistry of Materials & presented
at SPC E meeting, July 30, 2001, San Diego, CA

13. Is there a prototype? (If not, how much will it cost to build one) Is further development work needed? Is development now in progress? Scheduled? Dependent on commercial or federal sponsorship?

Yes

14. List commercial possibilities including quantities and sales price range, if available.

15. Please include an abstract of the invention. This will be used in our campaign to promote the invention, and should, therefore, be no longer than a typewritten page and not contain confidential information.

see attached

16. Certifications

I (we), undersigned hereby disclose to the Patent Committee of the University of Central Florida an invention which I (we) believe to be patentable and of which I (we) certify that I am (we are) the sole inventors.

I (we) request that the Patent Committee determine whether the University of Central Florida wishes to join in the development and exploitation of this invention.

I (we) authorize the Patent Committee to consult the opinion of professional research agencies, patent attorneys, and/or experts in the area with which this invention is concerned in order to determine its feasibility and patentability.

I (we) further certify that this disclosure is made in good faith and of my (our) free will, and all statements made herein are true and correct to the best of my (our) knowledge and belief.

Signatures of all parties claiming inventorship of and/or rights in this invention: (minors require countersignature by parent or legal guardian)

Signatures:

1 Ken D. Bufful date 9/19/01
2 _____ date _____
3 _____ date _____
4 _____ date _____

Witnesses:

1 _____ date _____
2 _____ date _____
3 _____ date _____
4 _____ date _____

Supporting Signatures:

Supervisor(s) of Inventor
Silvana Cunningham date 9-19-01
date _____

Chair of Patent Committee

_____ date _____

Vice President for Research

_____ date _____

**New photosensitive polymeric material for WORM optical data storage with two-photon
fluorescent readout**

Kevin D. Belfield

Department of Chemistry and School of Optics/CREOL, University of Central Florida, Orlando,
Florida 32816-2366

Abstract

We report image formation via photoinduced fluorescence changes in a polymeric medium with two-photon fluorescence readout of a multi-layer structure. A two-photon absorbing fluorescent dye possessing functional groups with differential basicity, (7-benzothiazolyl-9,9-didecyl-2,2-(N,N-diphenylamino)fluorene), underwent protonation in the presence of a photoinduced acid generator upon exposure to a broad-band UV light source or femtosecond near-IR laser irradiation. Solution studies demonstrated formation of monoprotonated and diprotonated species upon irradiation, each resulting in distinctly different absorption and fluorescence properties. The fluorescence of the original, neutral, fluorophore was reduced upon monoprotonation, leading to a concomitant increase in fluorescence at longer wavelengths due to the monoprotonated form. Experiments in polymer films demonstrate the changes in fluorescence properties of the fluorophores can be employed for a write-once read-many (WORM) data storage medium with two-photon fluorescence readout. Two-channel, two-photon fluorescence imaging provided both “positive” and “negative” image readout capability.

Introduction

Over the past 50 years, the field of organic photochemistry has produced a wealth of information, from reaction mechanisms to useful methodology for synthetic transformations. Many technological innovations have been realized during this time due to the exploits of this knowledge, including photoresists and lithography for the production of integrated circuits, photocharge generation for xerography, multidimensional fluorescence imaging, photodynamic therapy for cancer treatment, photoinitiated polymerization, and UV protection of plastics and humans through the development of UV absorbing compounds and sunscreens, to name a few.

The scientific basis of many of these processes continues to be utilized today, particularly in the development of organic three-dimensional optical data storage media and processes.

With the ever-pressing demand for higher storage densities, researchers are pursuing a number of strategies to develop three-dimensional capabilities for optical data storage in organic-based systems. Among the various strategies reported are holographic data storage using photopolymerizable media,¹ photorefractive polymers,² and two-photon induced photochromism³ to mention a few. It is known that fluorescent properties of certain fluorophores may be changed (quenched) upon protonation by photogeneration of acid⁴. We have reported two-photon induced photoacid generation using onium salts and short pulsed near-IR lasers in the presence of a polymerizable medium, resulting in two-photon photoinitiated cationic polymerization.⁵ The inherent three-dimensional features associated with two-photon absorption provides an intriguing basis upon which to combine spatially-resolved, two-photon induced photoacid generation and fluorescence quenching with two-photon fluorescence imaging.⁵

The quadratic, or nonlinear, dependence of two-photon absorption on the intensity of the incident light has substantial implications ($dw/dt \propto I^2$). For example, in a medium containing one-photon absorbing chromophores, significant absorption occurs all along the path of a focused beam of suitable wavelength light. This can lead to out-of focus excitation. In a two-photon process, negligible absorption occurs except in the immediate vicinity of the focal volume of a light beam of appropriate energy. This allows spatial resolution about the beam axis as well as radially, which circumvents out-of-focus absorption and is the principle reason for two-photon fluorescence imaging.⁶ Particular molecules can undergo upconverted fluorescence through nonresonant two-photon absorption using near-IR radiation, resulting in an energy emission greater than that of the individual photons involved (upconversion). The use of a longer wavelength excitation source for fluorescence emission affords advantages not feasible using conventional UV or visible fluorescence techniques, e.g., deeper penetration of the excitation beam and reduction of photobleaching, and is particularly well-suited for fluorescence detection in multilayer coatings.

Rentzepis *et al.* reported two-photon induced photochromism of spiropyran derivatives at 1064 nm.⁷ Analogous to single-photon absorption facilitated isomerization, the spiropyran underwent ring-opening isomerization to the zwitterionic colored merocyanine isomer. The merocyanine isomer underwent two-photon absorption at 1064 nm, resulting in upconverted fluorescence. However, spiropyrans are known to undergo photobleaching and photodegradation upon prolonged exposure, and hence are not suitable for long-term use. Nonetheless, an intriguing model for 3-D optical storage memory was proposed. An intriguing bacteriorhodopsin-based holographic recording media and process, using two-photon excitation, has been reported by Birge *et al.*⁸

We previously reported the synthesis and characterization of organic fluorescent dyes with high two-photon absorptivity.^{5, 9, 10} Several of these dyes also undergo substantial changes in the absorption and fluorescence spectral properties in the presence of strong acid, i.e., they undergo protonation, affording changes in their polarizability, absorption and emission maxima, and fluorescence quantum yields.¹¹ We wish to report results of the photoinduced protonation of fluorene dye **1** in liquid solution and polymer thin films (Figure 1), and subsequent 3-D imaging of multilayer polymer films via two-photon fluorescence imaging, resulting in a write-once, read-many (WORM) optical data storage system.

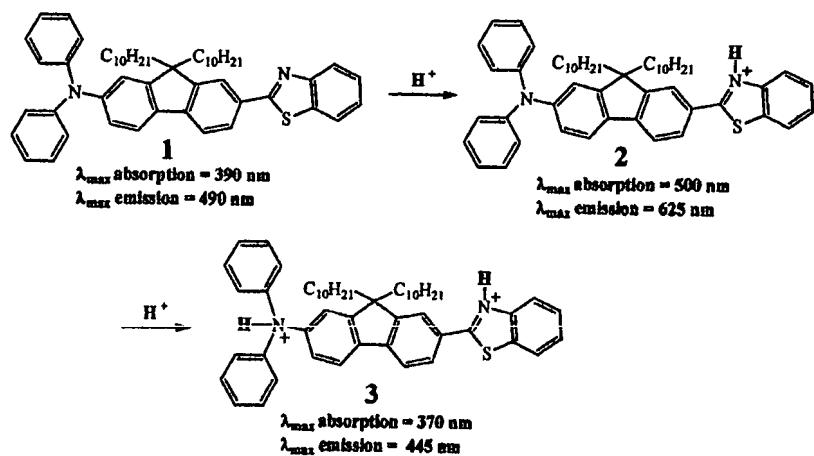


Figure 1. Reaction of fluorene **1** with acid, resulting in the formation of monoprotonated **2** and diprotonated **3** products.

Experimental Section

Materials. The photoacid generator, CD1010 (a triarylsulfonium hexafluoroantimonate salt as 50 wt% in propylene carbonate), was purchased from Sartomer and used as received. The synthesis and characterization of the two-photon absorbing fluorophore, 7-benzothiazoly-9,9-didecyl-2,2-(N,N-diphenylamino)fluorene, was described previously.⁹ Polystyrene (PS) (molecular weight 35,000) was purchased from Waters Associates and used directly. Phosphorylated poly(VBC-*co*-MMA) was prepared as previously reported.¹² Acetonitrile (ACN), 1,4-dioxane, and CH₂Cl₂ (HPLC or spectrophotometric grades) were purchased from Sigma-Aldrich and were used as received. Various masks were used during the photoexposure of prepared polymer films, including TEM grids (nickel square and hexagonal mesh grids from Polysciences), glass resolution targets (negative slide with the 1951 USAF test pattern from Edmund Scientific), and photolithographic waveguide masks (from PPM Photomask, Inc.).

Instrumentation. UV-visible absorption and fluorescence emission spectra from solutions were recorded with a Varian Cary 3 spectrophotometer and a Photon Technologies International (PTI) Quantamaster spectrofluorimeter fitted with one excitation monochromator (Xe lamp) and two emission monochromators (PMT detectors), respectively. Photoexposure of solutions and thin films were performed in a Rayonet photoreactor containing broadband UV bulbs (300-400 nm). Polymer thin films were spin-coated onto either No. 1 glass microscope cover slips or 2.5 x 2.5 cm microscope glass slides (Fisher) with a spin-coater from Headway Research, Inc. Film thickness of polymer films was measured with a Tencor Instruments profilometer. The two-photon upconverted fluorescence emission spectra of the fluorophore were recorded with the PTI spectrofluorimeter using a Clark-MXR CPA-2001 laser system. Femtosecond (fs) pulses from a frequency-doubled erbium-doped fiber ring oscillator were stretched to about 200 ps, then passed through a Ti:Sapphire regenerative amplifier and compressed down to 160 fs. The energy of the output single pulse (centered at $\lambda = 775$ nm) was 137 nJ at a 1 kHz repetition rate. This pumped a Quantronix OPO/OPA, producing fs pulsed output, tunable from 550 nm to 1.6 μ m. Two-photon fluorescence images of polymer films were performed on a modified Olympus Fluoview laser scanning confocal microscopy system equipped with a broadband, tunable Coherent Mira Ti:Sapphire laser (tuned to 800 nm, 115 fs pulselength, 76 MHz repetition rate), pumped by a 10 W Coherent Verdi frequency doubled Nd:YAG laser, and a two channel detection system (two

Hamamatsu photomultiplier tubes with band pass filters, channel 1: 510-550 nm, channel 2: 585-610 nm).

General procedures. All solution studies were performed in CH₂Cl₂. Individual stock solutions containing PAG only (1.7 wt%), polymer and PAG (18.3 and 1.7 wt%, respectively), PAG and fluorophore (1.7 and 0.16 wt%, respectively), and polymer, PAG, and fluorophore (18.3, 1.7, and 0.16 wt%, respectively) were prepared. From each stock solution, 25 μL was removed and placed into 10 mL volumetric flasks, then filled to volume. Solutions were transferred into a spectrofluorometer quartz cuvette cell fitted with a Teflon stopper and a small magnetic stir bar, which allowed for solution mixing during photoexposure to the broad-band UV light source in the Rayonet photoreactor. All solvents and solutions were deaerated by bubbling with N₂ gas prior to spectroscopic measurements, and were carefully protected from exposure to ambient or external light sources. Each solution was exposed for 120 s, with absorption and fluorescence emission spectra collected at 10 s intervals.

All polymer solutions (18 wt% polymer) were passed through a 0.45 μm glass filter, prior to spin-coating at a spin rate of 1500 rpm for 20 s. Films were dried under reduced pressure overnight, and their thickness measured by profilometry. Polymer film compositions typically contained 0.9 wt% of the fluorophore and 9 wt% of PAG, relative to the polymer. The dried films were then exposed to UV light for various durations through a mask and, following mask removal, the two-photon fluorescence imaging was performed on single and multilayered films.

Results and Discussion

Fluorene **1** was previously shown to undergo two-photon absorption and upconverted fluorescence on exposure to near-IR fs laser irradiation.^{5, 9} The two-photon absorbing dye **1**, contains basic nitrogen-containing benzothiazolyl and triarylarnino groups that are sensitive to the presence of acids. Pohers *et al.* have demonstrated the absorption spectrum of an acid-sensitive dye containing the benzothiazole group red shifts upon protonation in the presence of a photoacid generator (PAG).¹³ Due to differences in basicity (pK_b), fluorene **1** undergoes selective, stepwise protonation, first by protonation of the benzothiazolyl nitrogen then the triarylarnino nitrogen. This leads to a mixture of three species in Figure 1 (1, 2, and 3), each

with distinct UV-visible absorption and fluorescence emission properties. To understand the behavior of the two-photon absorbing fluorophore and predict results expected in solid thin film studies, solution studies were performed in CH_2Cl_2 . Time-dependent UV-visible absorption spectra for a solution containing **1** and the photoacid generator CD1010 (a triarylsulfonium salt) illustrate this nicely, as shown in Figure 2. Upon irradiation with broadband UV light (300-400 nm, 0.57 mW/cm^2), **1** undergoes protonation, resulting in formation of **2** whose absorption spectrum is red shifted by about 100 nm relative to that of **1**. The conversion of the neutral fluorophore **1** at early photolysis times (10 s) results in decreasing absorbance at its maximum at 390 nm, and increasing absorbance at 500 nm upon generation of the protonated form, **2**. The red shift was expected since fluorene **1** is of an electron donor- π -acceptor construct and protonation of the benzothiazolyl acceptor increases the electron deficiency of this group, affording a greater dipole moment and polarizability. When **2** undergoes protonation, a new absorption that is blue shifted relative to both **1** and **2** was observed, due to the fact that the once electron-donating diphenylamino group in **1** and **2** has been converted to an electron accepting moiety (quaternary ammonium salt) in **3**. The absorption due to the triarylsulfonium salt ($\lambda_{\text{max}} = 310 \text{ nm}$) also decreases with time as expected but, for clarity, is not displayed in Figure 2.

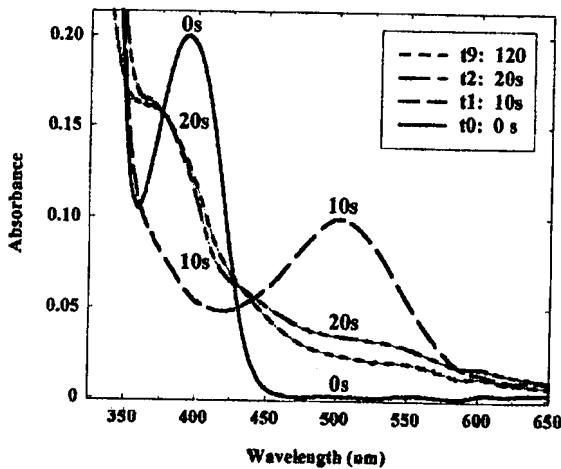


Figure 2. Time-dependent UV-visible absorption spectra of the photolysis of **1** and photoacid generator in CH_2Cl_2 at photolysis times from 0 to 120 s.

Changes in the fluorescence emission spectra corresponded with the observed changes in the absorption spectra. Protonation of **1** also resulted in a reduction of its fluorescence emission, while emission at longer wavelengths was observed due to excitation of the longer wavelength absorbing monoprotonated **2** (Figure 3). As can be seen, the fluorescence emission intensity at ca. 490 nm (390 nm excitation wavelength) decreases with irradiation while, at early photolysis times, emission at ca. 625 nm appears, which then blue shifts upon further protonation to **3**. The emission at 625 nm is from monoprotonated **2** upon excitation at 500 nm. Eventually, diprotonation results in a relatively weak, blue shifted emission at ca. 445 nm (from **3**). Thus, in addition to observing fluorescence quenching at ca. 490 nm, fluorescence enhancement (creation) at longer wavelengths (ca. 625 nm) is observed upon short photolysis times. As demonstrated in the following section, this behavior facilitates two-channel fluorescence imaging, resulting in contrast due to fluorescence quenching at the shorter wavelengths ($\lambda_{\text{emission}}$ of **1** from 425 – 620 nm) and fluorescence enhancement at longer wavelengths ($\lambda_{\text{emission}}$ of **2** from 520 – 700 nm).

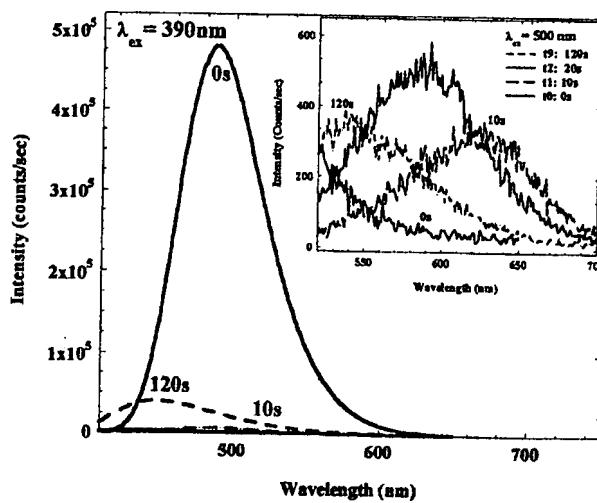


Figure 3. Time-dependent fluorescence emission spectra for the photolysis of **1** and photoacid generator in CH_2Cl_2 at photolysis times from 0 to 120 s (excitation at 390 nm). Inset shows fluorescence at longer wavelength with excitation at 500 nm.

To demonstrate the ability of fluorene 1 to exhibit two-photon upconverted fluorescence emission, fluorescence spectra were recorded upon excitation at a number of wavelengths using fs near-IR excitation. Two-photon upconverted fluorescence spectra (2.5×10^{-4} M, ACN) pumped with fs pulsed, near-IR are illustrated in Figures 4a and b. The neutral fluorophore 1, displayed upconverted fluorescence emission over a wide pump range, from 680 to 880 nm (Figure 4a) while, from figure 4b, it is readily apparent that maximum two-photon upconverted fluorescence intensity was observed when pumped at 800 nm. To further confirm that 1 underwent two-photon absorption, the total integrated fluorescence intensity was determined as a function of incident intensity (pump power). Fluorescence from a two-photon absorption process will exhibit a quadratic dependence on incident intensity. Indeed, Figure 5 confirms that fluorene 1 underwent two-photon absorption as evidenced by the quadratic relationship between fluorescence emission intensity at several pump powers at two different pump wavelengths.

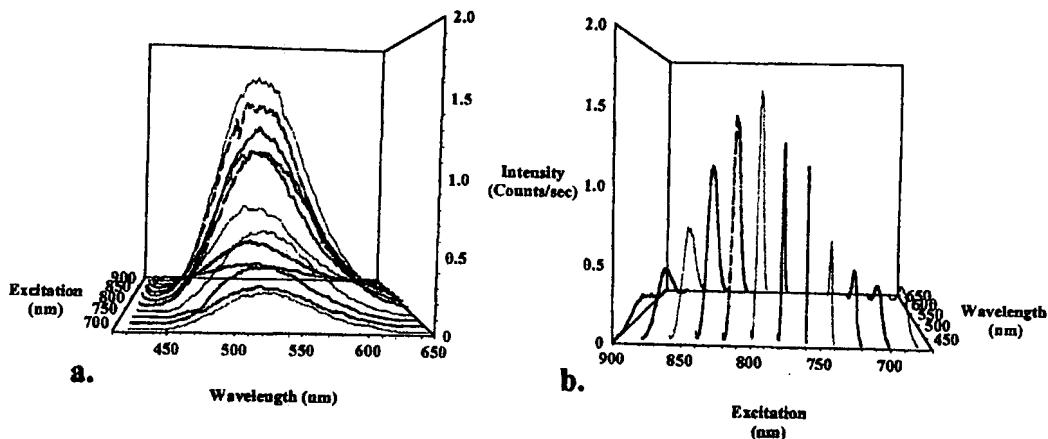


Figure 4. Two-photon upconverted fluorescence emission spectra of 1 at several fs pulsed pump wavelengths (2.5×10^{-4} M, ACN).

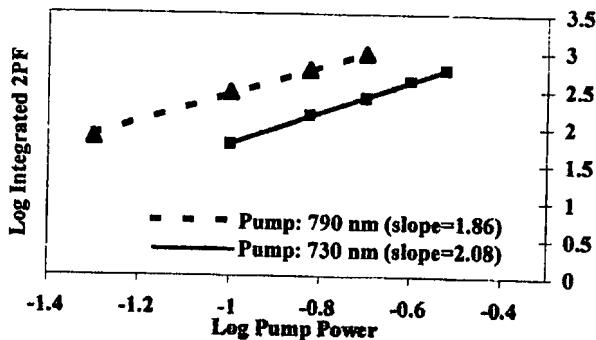


Figure 5. Plot of the total integrated fluorescence intensity of **1** as a function of pump power at two fs pump wavelengths.

Next, thin polymer films (ca. 2-3 μm film thickness) were prepared by spin coating (on glass) a mixture of fluorene **1**, the photoacid generator, and polystyrene or alternatively, phosphorylated poly(VBC-*co*-MMA) in a 1:3 v/v solution of acetonitrile/dioxane.¹⁴ Films were exposed to UV light through a number of different masks, including TEM grids, Air Force resolution targets, and photolithographic waveguide masks (Figure 6). After mask removal, two-photon fluorescence image collection was performed on the exposed films in single or multilayers.

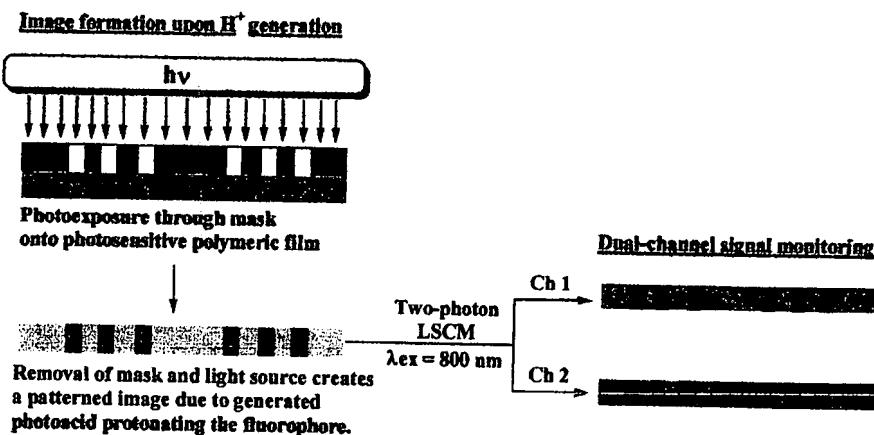


Figure 6. Diagram of image formation within a photosensitive polymeric film containing PAG, and acid-sensitive fluorophore, allowing two-photon induced, dual-channel fluorescence imaging.

Results analogous to those obtained in solution studies were observed but, quite fortuitously, the slower acid generation/protonation rate resulted in formation and stabilization of monoprotonated fluorene 2. With the beam focused in the plane of the fluorophore-containing layer, fluorescence intensity was recorded with both channel 1 (green) and channel 2 (red) simultaneously. The contrast in the “green” channel was due to the decrease in fluorescence of fluorene 1 (whose concentration decreases with irradiation). Contrast in the “red” channel was due to the fluorescence of monoprotonated 2 (whose concentration increases with irradiation).

Figures 7a and b show films exposed using an Air Force image resolution target with images recorded by both channels. The large differences in fluorescence intensity in exposed and unexposed regions can be clearly seen in the graph (Figure 7c) as well as the reverse parity of the images in the two channels, i.e. “positive” and “negative” image formation from one system. Time-dependent studies were performed by irradiating the films for various exposure times to determine the optimal contrast for each detection channel. The fluorescence intensity profiles as a function of exposure time and position across one set of the elements for each image is shown in Figures 8a and b. Optimal exposure time can be established by identifying the intensity profile that would provide the best signal-to-noise ratio, minimizing the hazard of overexposing films that may compromise resolution due to acid diffusion.

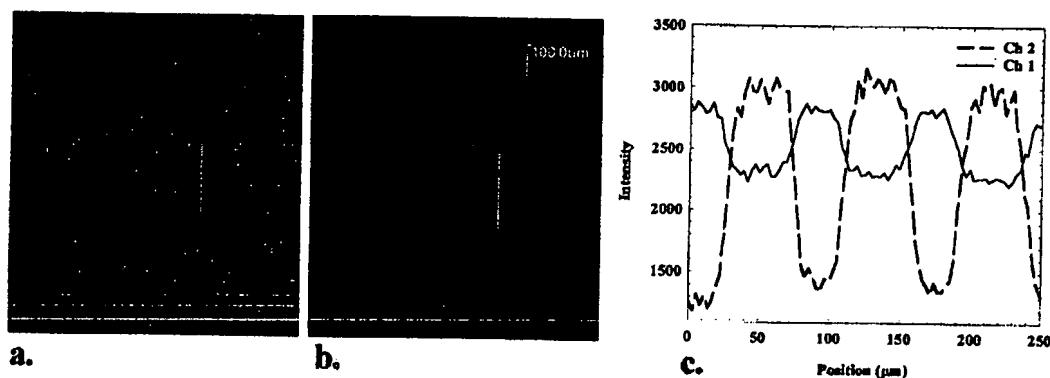


Figure 7. Two-photon fluorescent images of photosensitive films developed (via 350 nm broadband exposure, 4.4 mW/cm^2) using an Air Force resolution target mask. (a) Image recorded by channel 1, (b) image recorded by channel 2, and (c) fluorescence intensity by scanning an xy line across one set of three-member elements (yellow line across set 5).

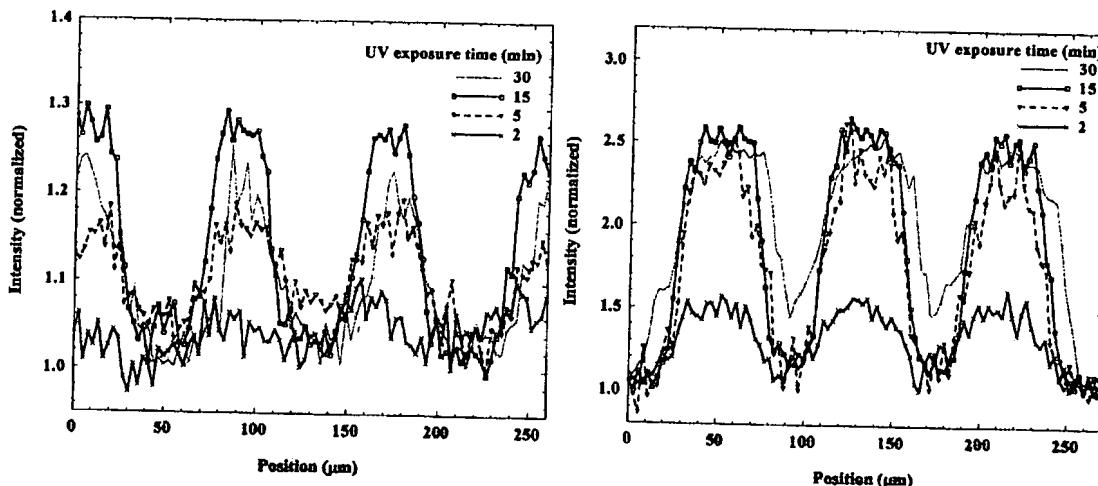


Figure 8. Fluorescence intensity plots versus position (xy line across a three-member element) as a function of exposure time. (a) Intensity monitoring with channel 1 (fluorescence decreases in exposed areas over time), and (b) intensity monitoring with channel 2 (fluorescence enhancement in exposed areas over time) clearly shows the reverse parity of the signals.

For demonstrative purposes, multilayer assemblies were constructed by placing an uncoated glass cover slip between two cover slips coated with patterned photosensitive films, with the coated sides against the middle cover slip (Figure 9). Three-dimensional two-photon fluorescence imaging was performed on the multilayer structures.

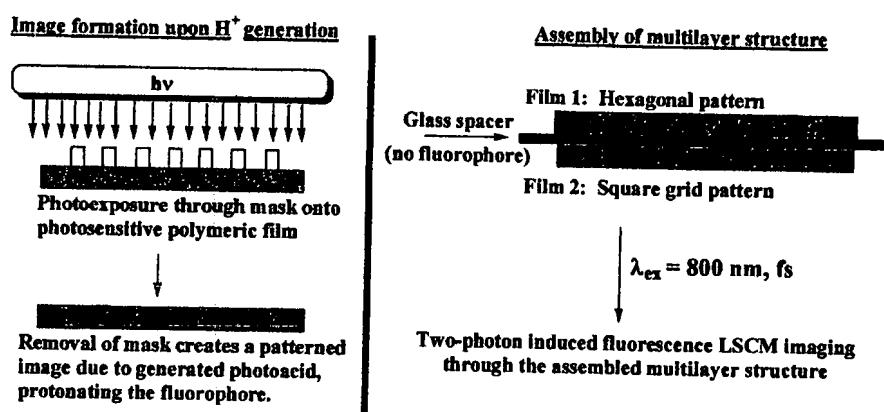


Figure 9. Image formation (upon photoacid generation) within photosensitive polymer films for assembly of multi-layered structures. Two-photon fluorescence LSCM imaging using fs pulsed near-IR pump allows for 3-D volumetric imaging of the layered structure.

Two-photon fluorescent images of the photosensitive films constructed in a multi-layer configuration (developed via UV exposure through TEM square and hexagonal grid masks) are displayed in Figure 10a. An xy planar scan of each film (hexagonal grid image on the top and square grid image on the bottom) within the multi-layer, by focusing and scanning within the plane of the films, clearly shows the photo-patterned image resulting from formation of the protonated species in exposed areas. A cross-sectional scan, where an xy line scan is stepped in the z dimension (multi-layered image between the grid images in Figure 10a), clearly displays the separate film layers and demonstrates the three dimensional nature of image formation possible within layered assemblies, and the nondestructive optimal sectioning ability of two-photon fluorescent imaging. The signal readout (Figures 10b and 10c) establishes the possibility for a WORM binary optical data storage medium, where the valleys can be designated as a "0" and the peaks a "1".

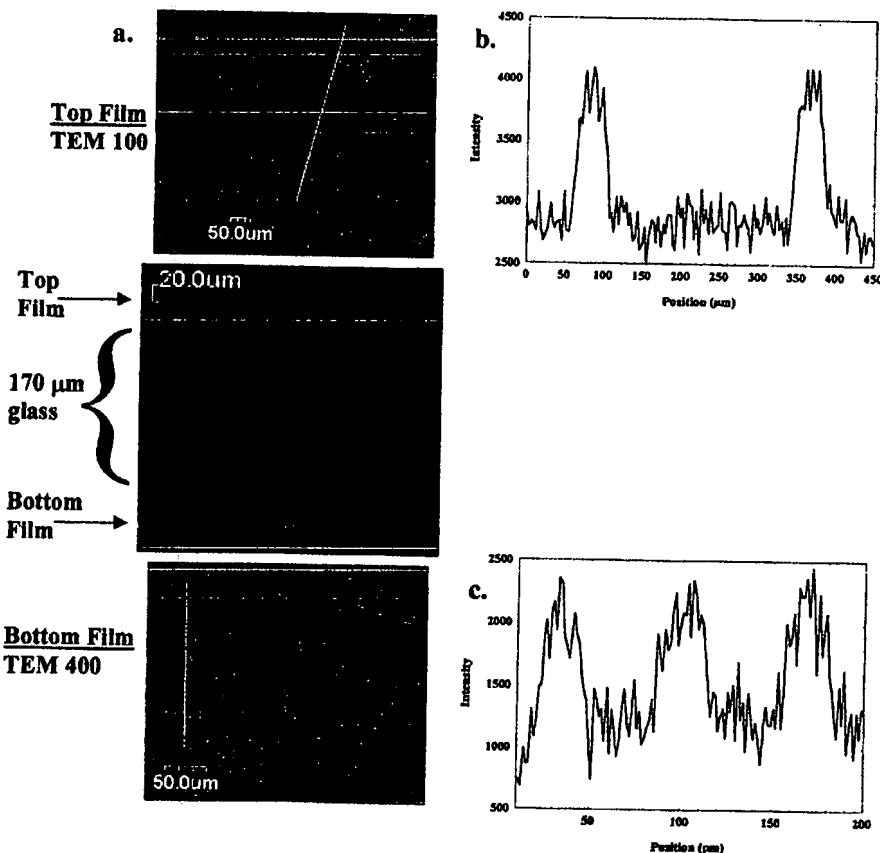


Figure 10. (a) Two-photon fluorescent images of multi-layered films developed via 350 nm, broadband irradiation (6.0 mW/cm^2) by exposure through TEM hexagonal and square grid masks. Fluorescence intensity plots for a line scan across a region (as defined by the yellow line across the image area) provides (b) image readout in one layer, and (c) changing the depth (z position) for image (signal) readout in the lower layer within a multi-layered system.

Finally, both writing and recording were accomplished by two-photon excitation of a fluorophore/PAG photosensitive polymer film in which writing was accomplished by xy-scans at 740 nm (115 fs, 76 MHz). The written image was read by a two-photon fluorescence imaging at 800 nm (115 fs, 76 MHz), as shown in Figure 11. Thus, image writing and reading has been accomplished via near-IR two-photon excitation of polymer films containing fluorophore 1 and a photoacid generator. The behavior and relative stability of 1 makes this compound a good candidate for WORM three-dimensional memory systems with writing and reading accomplished via two-photon fluorescence imaging.

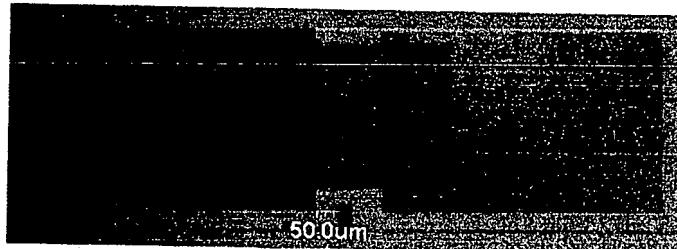


Figure 11. Image written (740 nm) and read (800 nm) in a photosensitive polymer film (1.5 μm) via a two-photon excitation.

Acknowledgments

The National Science Foundation (ECS-9970078, DMR9975773), the Research Corporation, and the donors of The Petroleum Research Fund of the American Chemical Society are gratefully acknowledged for support of this work. Profs. Eric W. Van Stryland and David J. Hagan are acknowledged for providing assistance.

References

1. See e.g., Cheben, P. and Calvo, M. *Appl. Phys. Lett.* **2001**, *78*, 1490.
2. See e.g., Belfield, K. D.; Chinna, C.; Najjar, O.; Sriram, S.; Schafer, K. J. in *Field Responsive Polymers, ACS Symposium Series 726*, Khan, I. M.; Harrison, J. S. (eds.), American Chemical Society, Washington, D.C., 1999, Chapter 17.
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14. Photosensitive polymer film compositions typically contained 0.9 wt.% of fluorene 1 and 9 wt.% of CD1010 relative to the polymer.

Date and hour of receipt: 11/18/02

**University of Central Florida
Invention Disclosure Form**

1. Title of Invention (brief, but comprehensive, technically accurate and descriptive):

Two-Photon Fluorescence Ternary Optical Data Storage

2. Inventors (full name, title, nationality, address (work and home), phone of inventor or inventors):

a. Kevin D. Belfield

Nationality USA

b.

Nationality _____

c.

Nationality _____

d.

Nationality _____

3. Financial Support/Contract Identification: Identify the specific grant or contract number (not the account number) and the external sponsors (governmental agencies, industrial sponsors, private agencies, or others), which provided support used to defray the costs related to the research from which the invention resulted. This information is needed to determine whether this invention is subject to any conuniments or restrictions arising from the terms of sponsorship.

No sponsors prior to the invention. Support has recently been received through an Army SBIR on High Density Optical Data Storage with Triton Systems, Inc.

4. List any existing agreements regarding this technology. Identify any and all agreements involving this technology. To include: research agreements, confidential disclosure agreements, consulting agreements, material transfer agreements, visiting scientists agreements or other agreements which are in place.

Confidential disclosure with Triton Systems, agreement to develop the technology with Triton Systems through the phase 1 SBIR.

5. Concise description of the invention: Your disclosure should enable someone having knowledge of the field to understand the invention. Include all essential elements (features, concepts, or new results of the invention, whichever is most applicable), their relationship to one another, and their mode of operation. Identify the elements, which are considered novel. Also, if the invention is an apparatus or system, attach drawings or a sketch and indicate if it has ever been built or tested. Use additional pages if necessary, attach drawings, manuscripts, papers, or other supporting material to facilitate understanding of the invention.

The innovation disclosed herein is a three-dimensional storage system that relies on a ternary data encoding scheme to achieve high data storage densities. The absolute fluorescence emission intensity recorded by one channel will be used to read a "0" or "1" with an appropriate threshold set. This will provide binary encoding. The ratio of fluorescence emission detected by each of two channels (set to record the emission at different wavelength regions corresponding to two different species in the recording medium) will be writing intensity dependent and will provide the "?" for "0", "1", and "?" ternary data encoding. The ternary data encoding is expected to increase data storage density by 50%. Thus, this technology combines all of the three-dimensional (3-D) spatially-resolved and deep writing/readout advantages associated with two-photon excitation/writing and two-photon fluorescence readout with the innovation made possible using these particular types of materials for ternary data encoding.

6. **Background:** In order for patent counsel to determine the patentability of this invention, it will be necessary to compare it to existing technology (referred to as "prior art"). This section should provide information to aid in the evaluation.

- a. List any published material such as patents, commercial literature, scientific articles relating to the invention.
- b. Identify the advantages or benefits of the invention over currently available technology, such as efficiency, cost benefit, simplicity, overcoming a defeat.
- c. Identify possible uses or new uses of the invention.
- d. What is the deficiency in the prior art, which your invention improves upon, or the limitation, which it extends?

see attached

7. Date and place at which discovery was made:

May 2002, UCF

8. Names and address of persons familiar with your work on this invention.

Katherine J. Schafer, Dept. of Chemistry, UCF

9. What do you see as the commercial use of your invention?

Possible new high density information storage medium

10. What firms/companies do you think may be, or are, interested in it; and why?

Triton Systems, Inc. is definitely interested since we already have been awarded (notified on 11/14/020 a phase 1 SBIR grant.

11. What do you see as the greatest impediment to the adoption of your invention?

The current industry standards but these are changing

12. **Public Disclosure/Publication Plans:** Public disclosure involves abstracts, and presentations at scientific meetings (including poster sessions), public seminars, shelving of thesis, publications, disclosure to others outside the University who have not signed a confidentiality agreement, and use, sale, or offer of sale of the invention. Identify dates and circumstances of any such disclosures. Also, indicate your future disclosure or publication plans, and notify the Office of Technology Transfer if the invention becomes publicly disclosed or published (whether by plan or inadvertently).

none yet

13. Is there a prototype? (If not, how much will it cost to build one) Is further development work needed? Is development now in progress? Scheduled? Dependent on commercial or federal sponsorship?

No prototype yet. In phase 1, we will demonstrate feasibility of a multilayer system and submit a phase 2 proposal. In phase 2 prototypes will be fabricated.

14. List commercial possibilities including quantities and sales price range, if available.

comparable in quantity and price to recordable DVDs

15. Please include an abstract of the invention. This will be used in our campaign to promote the invention, and should, therefore, be no longer than a typewritten page and not contain confidential information.

16. Certifications

I/we), undersigned hereby disclose to the Patent Committee of the University of Central Florida and invention, which I/we believe to be patentable and of which I/we certify that I am (we are) the sole inventors.

I/we request that the Patent Committee determine whether the University of Central Florida wishes to join in the development and exploitation of this invention.

I/we authorize the Patent Committee to consult the opinion of professional research agencies, patent attorneys, and/or experts in the area with which this invention is concerned in order to determine its feasibility and patentability.

I/we further certify that this disclosure is made in good faith and of my(our) free will, and all statements made herein are true and correct to the best of my(our) knowledge and belief.

Signatures of all parties claiming inventorship of and/or rights to this invention (minors require countersignature by parent or legal guardian):

1. _____ Date _____
2. _____ Date _____
3. _____ Date _____
4. _____ Date _____

Witnesses:

1. _____ Date _____
2. _____ Date _____
3. _____ Date _____
4. _____ Date _____

Supporting Signatures:

Supervisor(s) of Inventor

Date _____
Date _____

Chair of Patent Committee

Date _____

Vice President for Research

Date _____

Two-Photon Fluorescence Ternary Optical Data Storage

Kevin D. Belfield

Abstract

The data storage capacity is limited by the optical resolution of a system. In CD/DVD systems, an increase in the aerial data density has been primarily achieved by decreasing the bit dimension. However, the size of the optical spot (bit) is restricted by limitations imposed by the diffraction of light (Rayleigh criterion). Therefore, technologies that can effectively create and detect spot sizes beyond the diffraction limit (sub-Rayleigh) hold promise to achieving high-density optical storage.

The innovation disclosed herein is a three-dimensional storage system that relies on a ternary data encoding scheme to achieve high data storage densities. The absolute fluorescence emission intensity recorded by one channel will be used to read a "0" or "1" with an appropriate threshold set. This will provide binary encoding. The ratio of fluorescence emission detected by each of two channels (set to record the emission at different wavelength regions corresponding to two different species in the recording medium) will be writing intensity dependent and will provide the "2" for "0", "1", and "2" ternary data encoding. The ternary data encoding is expected to increase data storage density by 50%. Thus, this technology combines all of the three-dimensional (3-D) spatially-resolved and deep writing/readout advantages associated with two-photon excitation writing and two-photon fluorescence readout with the innovation made possible using these particular types of materials for ternary data encoding.

The technique proposed does not require the near field optics to achieve the sub-diffraction limited feature size. Our system will achieve sub-diffraction feature size through intensity dependent 2-photon processes. **Figure 1** illustrates the conceptual design of the 2-photon write/read system. The data is encoded in multiple layers, allowing data to be encoded with x, y, and z spatial coordinates. The 0-1-2 ternary code provides the potential to increase the storage densities by 50% relative to binary two-photon based technologies. Since the overall x-y storage area is fixed in the CD-DVD disk format at 120 mm (4.72 in) in diameter, more storage can be created on multi-layers in depth. Data storage of up to 1 terabit/in² can be achieved with multi-layer spacings of 30 μ m.

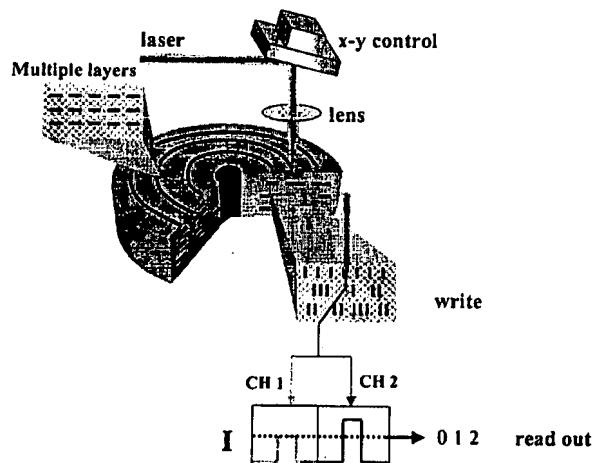


Figure 1. Conceptualized illustration of terabit/in² optical storage using ternary encoding 2-photon technology.

Introduction

The concept of this invention is a multilayer data storage system based on two-photon induced recording and two-photon fluorescence readout technology that consists of a ternary data-encoding scheme. Using a high numerical aperture (NA) objective lens, spatial resolution on the order of 120 nm is possible. This invention utilizes materials and processes disclosed for Belfield's previous binary write-once read-many (WORM) three-dimensional (3-D) optical data storage invention for which a Provisional U.S. patent was filed.¹ In this approach, photoinduced fluorescence changes in a polymeric medium are employed to a WORM data storage medium with two-photon fluorescence readout. Both image writing and reading will be accomplished via near-IR two-photon excitation of polymer films containing a fluorophore and photoacid generator (PAG). Furthermore, rather than using the previously disclosed binary encoding scheme, a ternary encoding scheme will be utilized, increasing the data storage capacity by 50%.

Table 1 summarizes the current state-of-the-art in optical data storage disks (CD-ROM and red DVD), and on a third in development (blue 2-layer DVD [expected to be on the market by 2005]).

Table 1. Storage Details for State of the Art Optical Storage Disks					
Disk Diameter = 120 mm = 4.72 in. DVD Hub = 0.85 in CD Hub = 1.81 in; Active Area = 14.0 in ² Active Area = 16 in ² , 2 Layers Thickness = 1 mm.					
Format	Gbytes Per Format	Gbits/in ²	Bits/ μm^2	Bit and Land Area (μm^2)	Bit and Land Width (μm)
CD ROM 1 Layer	0.600	0.344	0.533	1.87 μm^2	1.370
Red DVD 1 Layer	4.7	2.34	3.63	0.275	0.524
DVD 2- Layer	~ 10 ~ 5 per layer	5.0 2.5 per layer	7.75 3.87 per layer	0.129 0.258 per layer	0.507 per layer

Gbits/in² = [Gbytes/Format] x 8 (bits /byte) / Format area (in²)
 Bits/ μm^2 = [Gbits/in²] x 1.55 x 10⁻⁹ (in²/ μm^2)
 Bit and Land Area (μm^2) = [1/ Bits/ μm^2]
 Bit and Land width (μm) = Square Root Bit Area

Writing and Reading Optical Data

The write/read system using the two-photon technology is a five-part process. Part one involves the creation of the data storage medium; Parts two and three entail the data writing process; while Part four and five comprise the data reading process. The process is conducted using a near-IR laser to write and read data from a multilayered optical disk (Figure 2).

The recording medium is cast from a transparent polymer (polystyrene, PMMA, or polycarbonate) impregnated with a photosensitive Photo-Acid Generator (PAG) (commercially available "onium salt" that is currently used in photolithography) and a reactive dye (RD) (a stable fluorine dye).

In Part two, a near infra-red tunable Ti:Sapphire (Clark-MRX or Mira) laser is focused into the storage medium with a high intensity, short pulse at 730 nm (Figure 3). The depth of focus for the laser is able to be adjusted, yield the three-dimensional ability for data storage using this technique. The minimum spot size of the focused laser beam is the "diffraction limit" (DL) of the lens, also called the Rayleigh criterion limit, the "circle of confusion", or the Airy disk. The DL = (λ/NA) , where λ is the recording wavelength and the NA is the numerical aperture of the focusing lens. It is proposed, after the initial proof-of-concept, to utilize an NA = 1.4 to produce a smaller DL = 520nm. The photosensitive PAG molecules and the reactive dye (RD) in medium do not absorb 1-photon 730nm IR light at modest intensity (I), thus, allowing the 730nm photons to penetrate into the medium until the strength of the intensity squared (I^2) is very high. If ultraviolet light of (365nm) was utilized, it would enter the medium, be absorbed by the PAG to make excited PAG*, and also be absorbed by the polymer medium. This would prevent the deep penetration needed for multi-layer storage. The theory and practice of 2-photon absorption is that when the squared

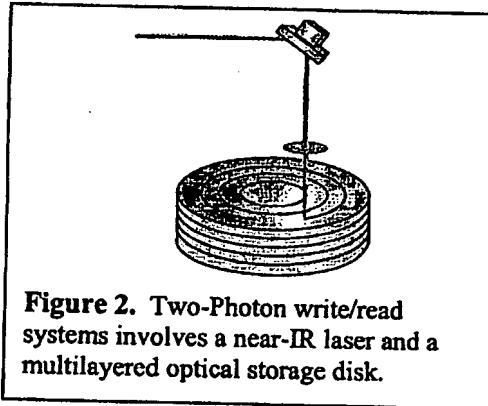


Figure 2. Two-Photon write/read systems involves a near-IR laser and a multilayered optical storage disk.

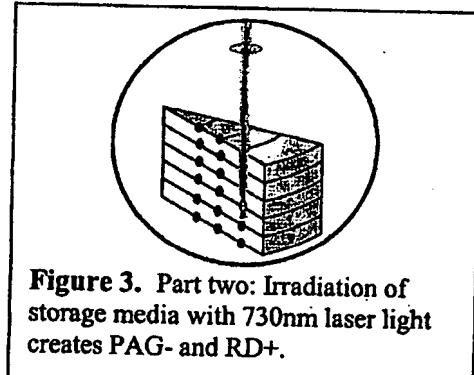
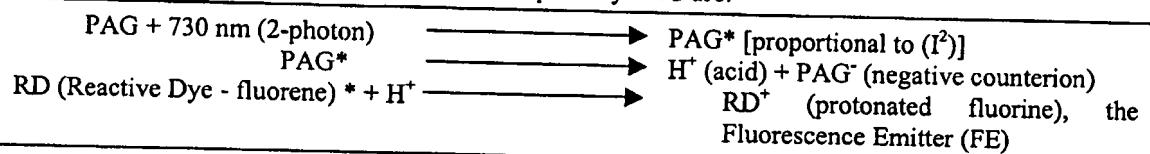


Figure 3. Part two: Irradiation of storage media with 730nm laser light creates PAG- and RD+.

intensity (I^2) is high enough, the PAG will absorb 2-photons at 730nm that will have the same energy as 1-photon at 365nm, and will be excited to PAG*. Because excitation by 2-photon absorption depends on I^2 rather than being linear with (I), we call 2-photon excitation a “non-linear optical” (NLO) effect. The sequences of reactions following 2-photon absorption by PAG are:



PAG is excited to PAG*. The PAG* yields a proton (H⁺) and donates it to RD, leaving PAG⁻, which is a stable negative counter-ion. RD becomes RD⁺, which is the protonated fluorene dye, a Fluorescence Emitter (FE).

The third part (Figure 4) of the process is the formation of the stable balanced ion pair from the negative counter-ion, PAG⁻, and the positive RD⁺. The stable ion pairs make-up the data storage “voxel” (volume pixel) in the medium. At this point of the process, the data has been encoded into the medium.

In Part 4 (Figure 5), the laser is retuned for data reading. Readout is performed by stimulating the fluorescence of FE and RD using a 2-photon laser light pulse (~10μs), thus ensuring deep penetration of the light to the desired depth. Since stimulation with 730nm light would excite more PAG and create more FE during reading, thus convolute the fluorescence readout, 800nm light is used. 800nm light will cause fluorescence of both FE and RD without exciting more PAG.

In Part 5 (Figure 6), the FE and RD, fluoresce at 650nm and 530nm, respectively. These two fluorescent output signals (lasting for ~5ns) give a unique advantage in data storage. These signals allow the reading of 3 pieces (ternary) rather than 2 pieces (binary) of information from each bit. This gives us a potential advantage of (3/2) or 50 % more data storage from the same number of bits over a binary system. As shown in Figure 1, Channel 2 (red from FE) produces “0” and “1”, while Channel 1 (green from RD) is taken as a ratio of the intensity of channel 1 to channel 2 to give the third bit noted as “2”.

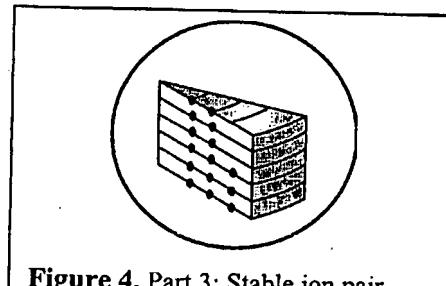


Figure 4. Part 3: Stable ion pair data storage “voxel” formed.

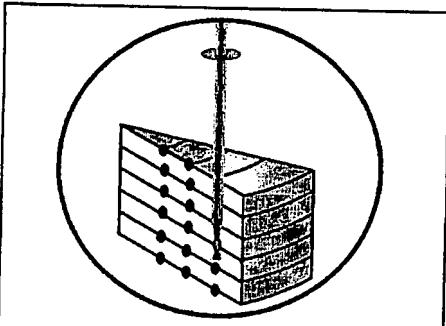


Figure 5. Part 4: Voxel is irradiated with 800nm laser light.

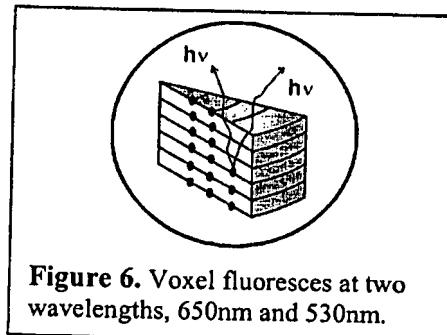
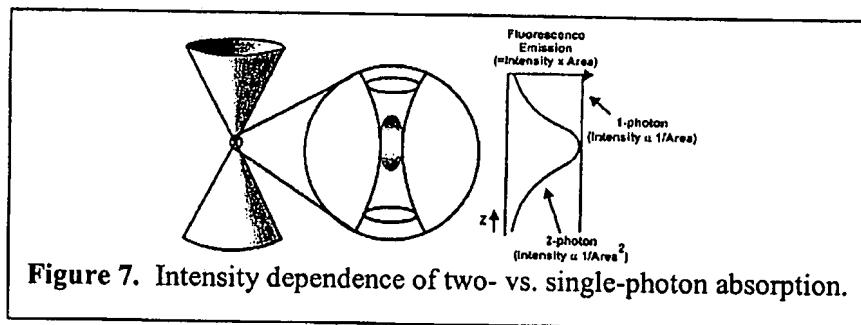


Figure 6. Voxel fluoresces at two wavelengths, 650nm and 530nm.

High Density Data Storage

The quadratic dependence of two-photon excitation on incident intensity relative to single-photon excitation is illustrated in Figure 7. The more highly localized two-photon excitation can be observed in the focal volume. The lower circle represents the diffraction limit spot made by the entering focused laser light. The cylinder of that diameter, labeled "1-photon (proportional to 1/Area)" is the cylindrical volume of the diffraction limit spot in depth that represents the linear absorption intensity of the entering light, and the area-volume of product that would be made by 1-photon absorption of ultraviolet light. The Gaussian curve of Figure 7 within the focal cylinder, "2-photon (intensity $\propto 1/\text{area}^2$)", is the distribution of light intensity squared (I^2). Since PAG does not absorb 1-photon light at 730 nm, and does not absorb 2-photon light until I^2 reaches a maximum, the focal volume has decreased to the smaller area at the middle of the two cones before 2-photon absorption occurs. The inner "voxel" (volume pixel) that is formed by the diffraction limited laser spot on or in the recording medium, and the sub-diffraction limit areas of the fluorescence emitter (FE) product are formed. Using a high numerical aperture (NA) lens, spatial resolution can be maximized, but the diffraction limit cannot be surpassed except for some modifications of point-spread functions. However, the nonlinear phenomenon of two-photon absorption can be exploited to produce sub-diffraction-limit spatial resolution, on the order of 120 nm using a high NA objective lens.^{2,3} Thus, even if the focal spot size for a given optical system (wavelength and objective lens) is larger than the diffraction limit, the diffraction limit can be exceeded provided that the photochemical processes responsible for the formation of voxels has a threshold response to excitation light intensity. The threshold is the level of light intensity above which the photochemical reactions become irreversible (e.g., permanent modification of fluorescence or refractive index). In this case, the diffraction limit becomes just a measure of focal spot size; it does not put any actual constraint on the voxel size. Recently Tanaka, Sun, and Kawata have measured the voxel sizes of 2-photon-created polymer and show voxel cross-section of 120 nm, compared to diffraction limit spots of 500 nm. This threshold performance depends on individual photochemical reactions and will be optimized for the proposed two-photon PAG/fluorophore system. Furthermore, if confocal 4π or adaptive optics are employed, spatial resolution on the order of 100 nm in both axial and lateral dimensions can be expected.⁴ If the voxel containing the fluorescent product of the 2-photon reaction remains sub-diffraction limit, and if it can be read out using diffraction limit readout optics, then we can achieve increased data storage by the use of closer packing of data in voxels of about 4-fold in area, which could reduce the number of layers needed for high density data storage by up to 4-fold.

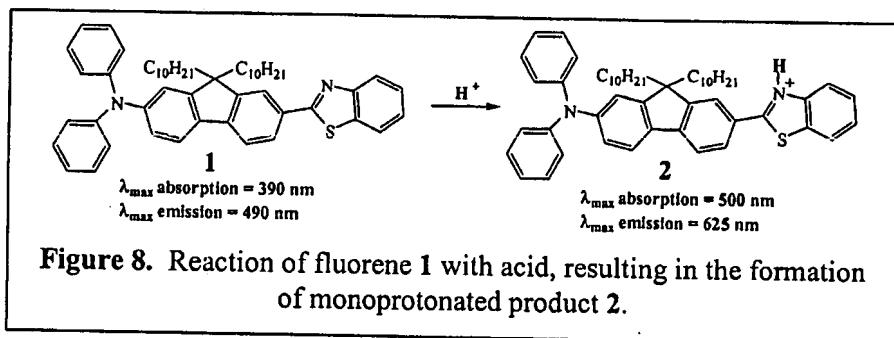


The inherent three-dimensional features associated with two-photon absorption provides an excellent basis upon which to combine spatially-resolved, two-photon induced photoacid generation and fluorescence quenching with nondestructive two-photon fluorescence imaging, eliminating the need for a fixing step. A significant advantage of this approach is that solutions for optical storage can take

advantage of new spatial and spectral dimensions. In addition, this multilayer approach provides optical memories that use the volume of the medium by recording data as binary (or ternary) planes stacked in 3-D. The use of transparent materials as storage media, allows for a large number of layers that can be used. The data is stored in discrete bits in the plane, but also through the volume. Relative to a one-photon-based process, much higher information densities can be obtained by writing multiple layers of bits; this is due to, first, the excitation light penetrates deeply into the material, and is absorbed only at the focal region, and secondly, Rayleigh scattering is reduced for the longer wavelengths used for two-photon excitation.

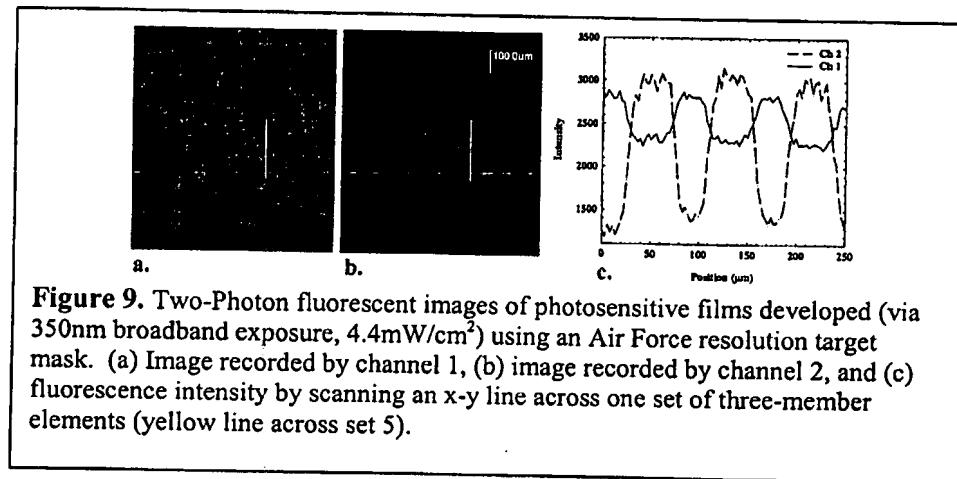
Two Photon Process Details

Figure 8 illustrates the chemical process yielding image formation within a photosensitive polymeric film containing PAG and an acid-sensitive fluorophore, which allows two-photon induced, dual-channel fluorescence imaging.



With the beam focused in the plane of the fluorophore-containing layer, fluorescence intensity is recorded with both channel 1 (green) and channel 2 (red) simultaneously. The contrast in the “green” channel is due to the decrease in fluorescence of fluorene 1 (whose concentration decreases with irradiation). Contrast in the “red” channel is due to the fluorescence of monoprotonated 2 (whose concentration increases with irradiation).

Figures 9a and 9b show films exposed using an Air Force image resolution target with images recorded by both channels. The large differences in fluorescence intensity in exposed and unexposed regions can be clearly seen in the graph (**Figure 9c**) as well as the reverse parity of the images in the two channels, i.e. “positive” and “negative” image formation from one system. Time-dependent studies were performed by irradiating the films for various times to determine the optimal contrast for each detection channel.



The innovation disclosed herein is a three-dimensional storage system that relies on a ternary data encoding scheme to achieve high data storage densities. The absolute fluorescence emission intensity recorded by one channel will be used to read a "0" or "1" with an appropriate threshold set. This will provide binary encoding. The ratio of fluorescence emission detected by each of two channels (set to record the emission at different wavelength regions corresponding to two different species in the recording medium) will be writing intensity dependent and will provide the "2" for "0", "1", and "2" ternary data encoding. The ternary data encoding is expected to increase data storage density by 50%. Thus, this technology combines all of the three-dimensional (3-D) spatially-resolved and deep writing/readout advantages associated with two-photon excitation writing and two-photon fluorescence readout with the innovation made possible using these particular types of materials for ternary data encoding.

The 2-photon technology proposed combines all of the three-dimensional (3-D) spatially-resolved and deep writing/readout advantages associated with two-photon excitation writing and two-photon fluorescence readout with the innovation made possible using these particular types of materials for ternary data encoding.

Background

Novel approaches to Optical Data Storage

Several novel approaches to overcome the limitations associated with surface storage by pits in CD-DVD and magneto-optical disc technology are currently in development. These novel technologies include near-field recording, solid immersion lens frequency/time domain optical storage, spectral hole burning, photon echo memory multilayer storage with transparent materials, two photon and fluorescent memories volume storage, page oriented holographic memories and bit-oriented microholographic discs. The storage potential of these novel approaches in comparison to current technology is summarized in **Figure 10**.

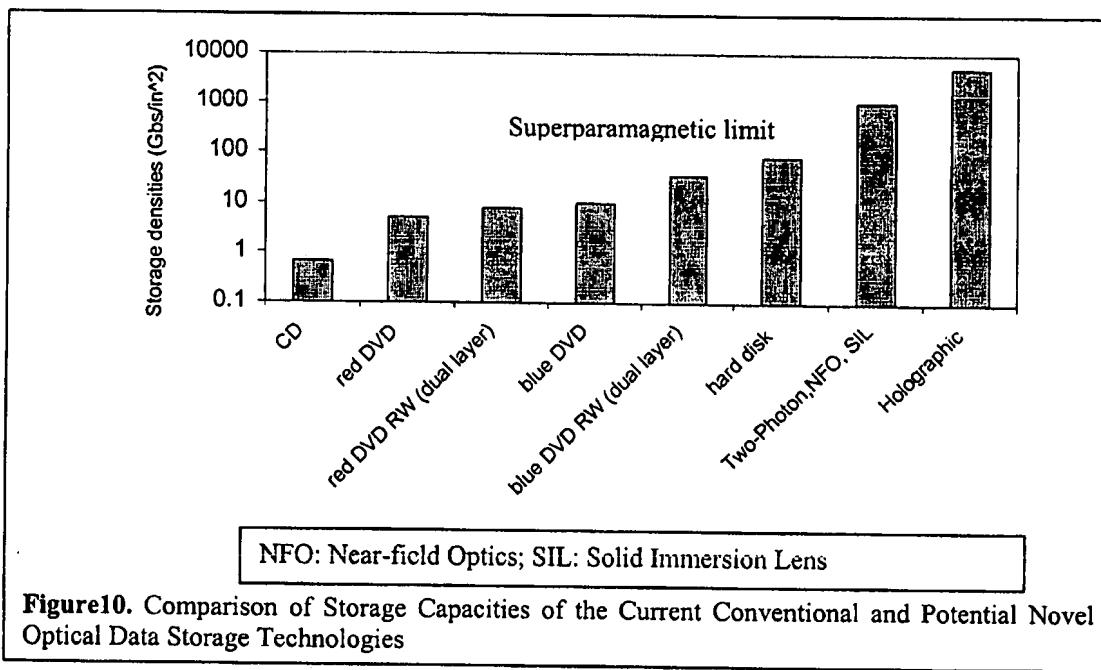


Figure10. Comparison of Storage Capacities of the Current Conventional and Potential Novel Optical Data Storage Technologies

Traditional (CD and DVD) optical data storage discs are encoded with 2-bit (binary) "pits" on the surface, created by laser ablation (burning) of light focused on the disk surface through a DL optical system. The un-pitted area is called the "land area". In calculations made here, the "bit area" that is calculated includes the bit and land area, and a "bit width", which includes the pit and land width

For readout, the bits are scanned by DL-focused "red" diode laser beam, much as in Figure 1. If the probed bit is transparent, the light goes through the transparent disk, is reflected back from the lower mirror, and returns to the photo-detector as a "1" bit. If the bit is opaque, the detector reads a "0" bit. The reflected signal light is usually collected through the same optics that transmitted the probing spot. The encoding converts 8 bits received to 14 bit words, which insures that the binary code for "1" is separated by no fewer than two binary "0"s. A collection of 8 bits creates one Byte, which is the coding element.

The ablation system is a surface process, and therefore multi-layer storage is not an option. A maximum of 2-layers (top and bottom) is possible.

- From Table 1, the CD-ROM stores 0.344 Gb/in² with pit widths of 1.370 μm
- From Table 1, the red DVD stores 2.34 Gb/in² with pit widths of 0.524 nm
- From Table 1, the blue DVD stores 5.0 Gb/in², which is twice the storage of the red DVD, but it has 2 layers or the same storage as the red DVD per layer.

Accordingly these disks are near the storage limit using near DL spots created by DL laser ablation and readout. Our 2-photon-fluorescent memory system will achieve increased storage assuming DL read-in and read-out, using multi-layers, and 3-bit data encoding versus 2-bit readout.

There are two directions that can be taken in order to improve the capacity of 2-D optical storage systems. The first applies to surface storage systems and would be to increase the area storage density by surpassing the limit imposed by the diffraction of light. The second option is to add a third dimension in the spatial, spectral or time domain. This is the approach taken by the novel technologies shown in Figure

10. Adding a new dimension increases both the capacity and data transfer rates tremendously. A third dimension can be added by using multiple data layers instead of one. In two-photon technology, for example, hundreds of layers can be assembled using transparent materials as storage media. The data is recorded in binary planes stacked in 3D. On the other hand, in holographic technology information is recorded through volume. Summaries of some of the major alternative approaches that are in various stages of development are shown in Table 2.

Table 2. Comparison of some of the novel approaches in optical storage with current CV-DVD technology

Approach	Pro's	Con's	Comments
UCFA Approach: Two-photon /fluorescence	<ul style="list-style-type: none"> Access to multiple data layers Potential for high aerial density 500-1000 gb/in² 	<ul style="list-style-type: none"> Requires optimization of photosensitive media 	Provides one further dimension in spatial, spectral, or time domain
Near field optical recording (NFOR)	<ul style="list-style-type: none"> Potential for very high aerial density (1000 Gb/in²) 	<ul style="list-style-type: none"> Low optical efficiency Difficult to satisfy high data transfer requirements 	Constrained to 2-D surface limitations
Solid immersion lens (SIL)	<ul style="list-style-type: none"> Higher efficiency than NFOR Potential for high aerial density of 1000 Gb/in² 	<ul style="list-style-type: none"> Requires extremely short working distance of lens to recording layer 	SIL in combination with NFR will enable high aerial densities
Holographic/ microholographic	<ul style="list-style-type: none"> Potential for extremely high bit density of >1000 Gb/in² Potential for very high-speed systems 	<ul style="list-style-type: none"> Media optimization required – problems with shrinkage, scattering etc Reproducibility of object beam is a problem 	Promising terabyte devices but technical hurdles have prevented its commercialization

Estimation of Number of Layers Needed to Achieve 1.0 Tbit/in² Storage Density

Above we estimated the approximate number of data storage layers that would be needed to store 1 Tbit/in² of data at the storage density of the CD-ROM and the red DVD, and we found we would need about > 1000 layers for the CD-ROM, and about 400 layers for the red or blue DVD. In Table 3 we show our calculation in more detail for various storage densities up to 1.0 Terabit/in², under the following assumptions:

1. The working area is 14 in², assuming CD-ROM format (DVDs are at 16 in²)
2. Our bit widths will be > 520 nm, to stay above the DL of an 800 nm photon focused with a 1.4 NA lens.

3. The calculated bit widths include the land areas – there may be a 2- to 5- fold error in these calculations
4. We assume binary (2-bit) readout, but include 3-bit (ternary) readout with $(3/2) = 1.5$ or 50 % more bit information than the actual number of bits.
5. We do not include the extra storage we might realize from the small voxel bits of information that we may see in 2-photon recording, because it is not clear that we can read these small voxels out with our DL 2-photon IR laser.

The calculations, using 10 Gbytes/in² in 1 and 5 layers as an example are:

$$\text{Total Gbytes/in}^2 = [\text{Total bites}/\mu^2] / (1.55 \times 10^{-9} (\text{in}^2/\mu^2)); \quad \text{Total} = 10 \text{ gb/in}^2$$

$$\text{Total bits/m}^2 = 1.55 \times 10^{-9} \times \text{Gbytes/in}^2 \quad \text{Total} = 15.5 \text{ bits/in}^2$$

$$[\text{Gbytes/in}^2] / \text{layer} = [\text{Total Gbytes/in}^2] / \text{number of layers} \quad 2 \text{ Gb/in}^2 / \text{layer for 5 layers}$$

$$[\text{bits}/\mu^2 / \text{layer}] = \text{Total bits}/\mu^2 / \text{number of layers} \quad 3.1 \text{ bits/in}^2 / \text{layer for 5 layers}$$

$$\text{Bit area } (\mu^2) = 1/(\text{bits}/\mu^2); \quad 0.0645 \mu^2 \text{ for 1 layer, } 0.322 \mu^2 \text{ for 5 layers}$$

Table 3 Data Storage (Gbytes) and Data Storage Density (Gbytes/in²)

Using 2-Photon Recording and Readout in Multiple Layers 20 layers can store up to 75 Gbytes/in²

Format	Layers	Storage per CD Gbytes	Storage Density Gbytes/in ²	Bit Length (μ)
CD ROM	1	0.600	0.344 Gbi/in ²	1370 nm
Red DVD	1	4.7 GBy	2.34 Gbi/in ²	0.524 μ
2-Photon				
2-bit Read	5	17.5	10	0.576
3-bit Read	5	26	15	0.576
2-bit Read	10	35	20	0.576
3-bit Read	10	52	30	0.576
2-bit Read	50	175	100	0.576
3-bit Read	50	260	150	0.576
2-bit Read	300	1.22 TByte	700	0.526
3-bit Read	300	1.83 TBit	1.050 Tbit	0.526
2-bit Read	500	1.75 TByte	1.000 Tbit	0.576
3-bit Read	500	2.62 TBit	1.500 Tbit	0.576

50 to 200 layers can store 100 to 750 Gbytes/in²

300 to 500 layers are needed to store 700 to 1000 Gbytes/in²

References

1. Belfield, K. D.; Schafer, K. J. "A New Photosensitive Polymeric Material for Optical Data Storage using Multichannel Two-Photon Fluorescence Readout" *Chemistry of Materials* 2002, 14, 3656-3662.
2. Tanaka, T.; Sun, H.-B.; Kawata, S. "Rapid sub-diffraction-limit laser micro/nanoprocessing in a threshold material system" *Appl. Phys. Lett.* 2002, 80, 312-314.

3. Sun, H.-B.; Tanaka, T.; Takada, K.; Kawata, S."Two-photon photopolymerization and diagnosis of three-dimensional microstructures containing fluorescent dyes" *Appl. Phys. Lett.* **2001**, *79*, 1411-1413.
4. Kawata, S.; Sun, H.-B.; Tanaka, T.; Takada, K. "Finer features for functional microdevices" *Nature* **2001**, *412*, 697-698.

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P. 01

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Inventor : Kevin D. Belfield
Appl. No. : 10/821,755
Filing Date: April 09, 2004
Art Unit : 1756
Examiner : Martin J Angebranndt
Docket No. : UCF-385
Customer No. : 23717
Title : Two-Photon Fluorescent Ternary Optical Data Storage

Mail Stop Petitions
Commissioner for Patents
P.O. Box 1450
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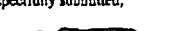
1. Petition under 37 CFR 1.78(a)(3) and 1.78(a)(6) for an Unintentionally Delayed Domestic Priority Claim (2 pages)
2. Application Data Sheet (3 pages)

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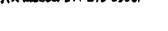
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Respectfully submitted,


Brian S. Steinberger
Attorney at Law
PTO Registration No. 36,423
101 Brevard Avenue
Cocoa, Florida 32922
(321) 633-5080 Facsimile (321) 633-9322

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